Enhanced H_2S Sensing Properties of Porous SnO_2 Nanofibers Modified with CuO

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Abstract:

Porous SnO_2 nanofibers were fabricated by electrospinning and oxygen plasma treatment. Subsequently, CuO was sputtered on the porous SnO_2 fibers as the modifier. H_2S sensing properties of the fibers were tested and the effect of CuO amount on the response and recovery characteristics to H_2S was investigated. It was found that the response is strongly dependent on the CuO amount and the response time and recovery time become longer with the increase of the CuO amount. The highest response of the fibers to 2 ppm H_2S attains 1.9×10^3 at the operating temperature of 100 with the optimum CuO thickness of 24 nm, and the fibers show good selectivity to H_2S.

Key words: SnO_2 nanofibers, electrospinning, CuO-modified, H_2S sensing

Introduction

Sensing materials based on p-type CuO and n-type SnO_2 have been reported showing high sensitivity and good selectivity to H_2S due to the formation of p-n junctions in air and the disruption of the p-n junctions by the conversion of CuO to CuS upon exposure to H_2S [1, 2]. Over the past decades, enormous efforts have been made to fabricate different kinds of H_2S sensing materials based on nanosized SnO_2 films and CuO films or particles by different methods [3-9]. However, the compacted films obstruct gas diffusion and adsorption and are not the best choice for gas sensing materials.

In recent years, one-dimensional nanomaterials, such as nanofibers, nanowires, nanoribbons and nanorods have been widely investigated for gas detection, and the sensitivity can be improved and response time can be shortened due to the high surface to volume ratio [10] and quantum confinement effect [11]. Hence considerable efforts have been made to fabricate one-dimensional H_2S sensing materials via thermal oxidation, thermal evaporation, hydrothermal process and electrospinning [10, 12, 13]. Xue et al. synthesized core/shell p-n junctions with hydrothermal SnO_2 nanorods as core and CuO nanoparticles as shell [10]. This core/shell junctions exhibited a high sensitivity about 9.4×10^2 and short response time about 30 s to 10 ppm H_2S at operating temperature of 60 . Kong et al. [12] fabricated CuO modified SnO_2 nanoribbons with thermal oxidation followed by mixing with CuO powders. It is reported that the sensor has high sensitivity (~180) and short response time (~15 s) to 3 ppm H_2S at room temperature. Vivek et al. obtained CuO doped SnO_2 nanowires by thermal evaporation [13]. The nanowires doped with proper concentration of CuO were reported exhibiting high sensitivity about 6×10^6 to 50 ppm H_2S at 150 .

In the present work, a novel method to fabricate CuO-modified porous SnO_2 nanofibers was proposed. Porous SnO_2 nanofibers were fabricated by electrospinning, followed by plasma treatment and annealing, and CuO were sputtered on SnO_2 nanofibers. The effects of the CuO amount on H_2S sensing properties of the prepared nanofibers were investigated.

Experimental

The electrospinning solution was prepared by dissolving 0.5 g polyvinylpyrrolidone (PVP, Sigma-Aldrich Trading Corp. Ltd., Mw=1.3×10^6 g/mol) and 1 g $SnCl_4 \cdot 5H_2O$ in 4 mL DMF (N, N-dimethyllformamide, Beijing Chemical Reagent Corp.) and 6 mL ethanol, and then sufficiently stirring at room temperature. The flow rate of the solution was 0.1 mL/h and the electrode-to-collector distance was settled at 4 cm. The optimized applied voltage was 8 kV. The fibers were deposited on a silicon based substrate which was embedded with a serpentine Pt heater and Pt interdigital electrodes [14].

The as-prepared fibers were dried for 4 h at 80 to ensure that the solvents were completely vaporized. Afterward, the fibers were treated with oxygen plasma of 0.28 W/cm^2 for 20 minutes at room temperature to modify the surface of fibers and form porous structure [14, 15]. After annealing at 660℃ for 4 h in ambient environment, SnO_2 nanofibers with porous structure were obtained.

CuO was deposited on porous SnO_2 nanofibers by rf magnetic sputtering. The Cu metal target (50 mm in diameter and 99.99% purity) was adopted and the substrate was kept at room temperature. The sputtering was carried out at a working gas pressure of 0.8 Pa in a mixture of Ar and O_2 (7: 3) with rf power of 50 W. The deposition rate is 18 nm/min and the thickness can be controlled by the deposition time. Finally, the modified fibers were annealed in air at 500 for 4 h with the ramp of 2 /min. The morphology of the fibers were examined by scanning electron microscopy (SEM, HITACHI S-4800), and the crystal structure of SnO_2 and CuO were examined by X-ray diffraction (XRD) which was conducted on a Philips X'pert Pro X-ray diffractometer with Cu Kα1 radiation (λ=1.5406 Å).

Gas sensing properties were measured using a static test system and current is employed to characterize the resistance of fibers. Dry synthetic air was used as both a reference gas and a diluting gas to obtain desired concentrations of H_2S. A certain volume H_2S with the concentration of 525 ppm was injected into the test chamber by a syringe through a rubber plug. After fully mixed with the diluting gas, the fibers were put into the test chamber. When the response reached a constant value, the fibers were taken out to recover in dry air. H_2S concentrations less than 0.5 ppm were obtained by secondary dilution. The response is defined as I_g/I_a, where I_a and I_g are the currents of the fibers upon exposure to dry air and H_2S, respectively. The response time is specified as the time to reach 90% of the maximum change of current after H_2S is injected. The recovery time is defined as the time to return to 10% of the maximum change of current after the removal of H_2S.

Results and discussion

The XRD pattern in Fig. 1 reveals all the major diffraction peaks of the SnO_2 and CuO after annealing. All the diffraction peaks can be perfectly indexed as the tetragonal rutile structure SnO_2 (JCPDS 41-1445) and the monoclinic structure CuO (JCPDS 05-0661), respectively.
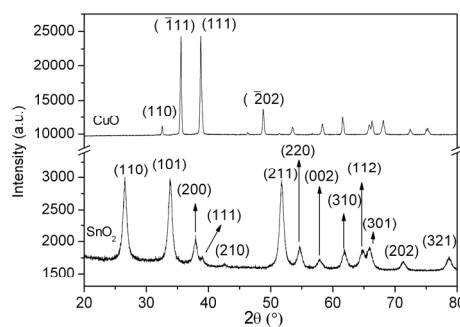

Fig. 1.　XRD patterns of SnO_2 nanofibers and CuO after annealing

In the work, samples of CuO-modified porous SnO_2 nanofibers with the CuO deposited for 0 s, 20 s, 40 s, 60 s, 80 s and 100 s, corresponding to the thickness of 0, 6 nm, 12 nm, 18 nm, 24 nm and 30 nm, are marked as 1[#], 2[#], 3[#], 4[#], 5[#] and 6[#], respectively.

Fig. 2(a) shows the SEM image of the porous SnO_2 nanofibers. It can be seen that the fibers show coarse morphologies with small particles and holes on the surface. During the oxygen plasma treatment, PVP was removed, resulting in a porous microstructure. The formation of the porous structure was proposed in our previous works [14, 15]. The SEM images of CuO-modified SnO_2 nanofibers with different CuO deposition times are shown in Fig. 2(b-f). It is clear that the porous structure of the fibers is maintained but the porosity decreases with the increase of the CuO deposition time due to the superfluous CuO.
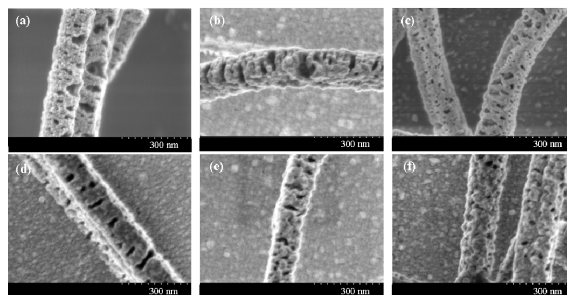

Fig. 2.　The SEM images of CuO-modified porous SnO_2 nanofibers with the CuO deposition time of (a) 0 s, (b) 20 s, (c) 40 s, (d) 60 s, (e) 80 s and (f) 100 s.

Fig. 3 shows the response of CuO-modified porous SnO_2 nanofibers with different CuO deposition time towards 2 ppm H_2S as the function of operating temperature. It can be seen that pure SnO_2 nanofibers are almost insensitive to H_2S at the operating temperature ranging from 30 to 170 . However, the responses of CuO-modified SnO_2 nanofibers increase with a raise of operating temperature, and attain the maximum value at about 100℃, then decrease with further raise of the operating temperature. In addition, it is apparent in Fig. 3 that the response of CuO-modified SnO_2

nanofibers is strongly dependent on the CuO amount, and it reaches the highest response (about 1.9×10^3) to 2 ppm H_2S with the optimum CuO thickness of 24 nm, then decreases quickly as the CuO thickness increased. The enhanced performance in CuO-modified porous SnO_2 nanofibers can be understood in terms of the formation of p-CuO/n-SnO_2 junctions on the surface of the fibers in air and disruption of junctions by the sulfurization of CuO into conductive CuS upon exposure to H_2S, which cause a large decrease in electrical resistance of the fibers [16].
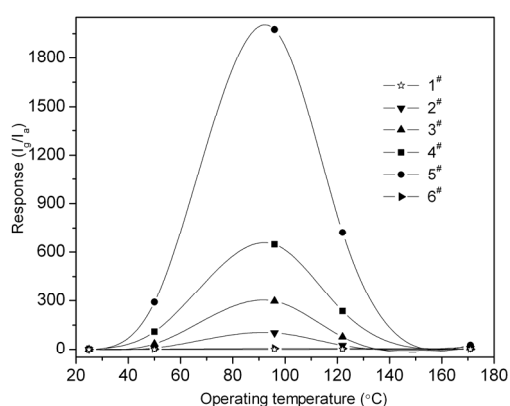

Fig. 3. *The response of the samples as a function of operating temperature.*

The sensing characteristics of SnO_2 nanofibers modified with different amount of CuO upon exposure to 2 ppm H_2S at optimal operating temperature of 100℃ were examined and the results are illustrated in Tab. 1. The slowdown of the response/recovery is observed with the increase of CuO deposition time.

Tab. 1: *Response time and recovery time of the samples to 2 ppm H_2S at 100℃.*

Sample number	1#	2#	3#	4#	5#	6#
Response time / s	-	50	65	100	115	180
Recovery time / s	-	22	22	26	30	40

Fig. 4(a) shows the response/recovery of sample 5# to H_2S from 0.01 ppm to 4 ppm at 100℃. The inset shows the response/recovery of the fibers to low concentration H_2S in magnified view. It is obvious that the current increase upon exposure to H_2S, and decrease rapidly and return to the original value after H_2S is removed. The response is about 0.9×10^3, and the response time and recovery time are about 105 s and 25 s upon exposure to 1 ppm H_2S, respectively. With the increase of H_2S

concentration, the response time became longer. The response of the fibers as a function of H_2S concentration when operated at 100℃ is shown in Fig. 4(b). For H_2S concentration of 0.01 ppm, the response is about 1.2 and the detection limit is less than 10 ppb. Moreover, the response rapidly increases with increasing of H_2S concentration, and there is an approximate linear relationship between the response and the concentration in the range of 0.01 ppm - 4 ppm.
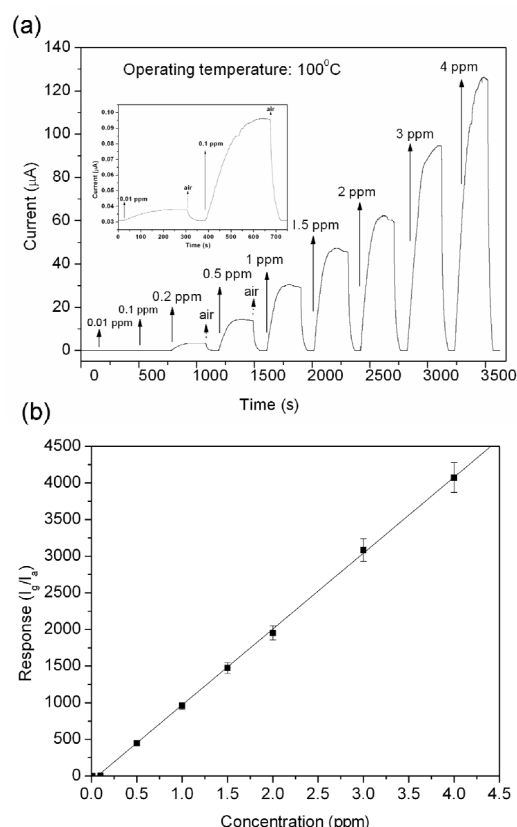

Fig. 4. *(a) The response/recovery of sample 5# to H_2S in the range of 0.01 ppm to 4 ppm at 100℃, (b) the response as a function of H_2S concentration.*

To investigate the selectivity of CuO-modified porous SnO_2 fibers to H_2S, the response of the fibers to interference gases including CH_3CH_2OH, SO_2, NO and CH_4 have been investigated. Fig. 5 depicts the response of sample 5# to 2 ppm H_2S and other pollutant gases with the concentration of 10 ppm at 100 ℃. The fibers are totally insensitive to interference gases and it shows that the porous SnO_2 nanofibers modified with optimal amount of CuO exhibit prominent selectivity to H_2S. The good selectivity of the fibers is attributed to the disruption of CuO-SnO_2 junctions upon exposure to H_2S.
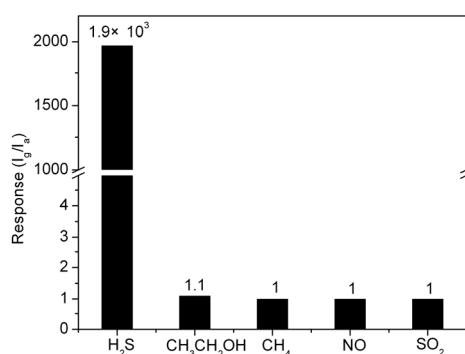
Fig. 5.   The selectivity of sample 5$^{\#}$ to H_2S.

Conclusion

A novel method to fabricate H_2S sensing materials based on CuO-modified porous SnO_2 nanofibers was explored. The porous SnO_2 nanofibers were fabricated with electrospinning followed by oxygen plasma treatment and annealing, then CuO was sputtered on the surface of the porous SnO_2 nanofibers. The CuO-modified fibers exhibit high response to low concentration H_2S at the operating temperature of 100℃, and the responses varied with the amount of CuO. The highest response of $1.9×10^3$ is obtained to 2 ppm H_2S at CuO thickness of 24 nm, and the response time and recovery time is about 115 s and 30 s. Furthermore, CuO-modified porous SnO_2 fibers show good selectivity to H_2S. The enhanced performance of the porous fibers is primarily due to the porous structure of fibers which was helpful to form CuO-SnO_2 junctions as many as possible in the surface of fibers.

Acknowledgements

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